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Discontinuity and quasitricritical behavior near T_c in ferroelectric triglycine selenate

Tomás Iglesias, Beatriz Noheda, Ginés Lifante, and Julio A. Gonzalo
Departamento de Física de Materiales, C-IV Universidad Autónoma de Madrid, 28049 Madrid, Spain

Marcel Koralewski
Institute of Physics, Adam Mickievichz University, 60-780 Poznan, Poland
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Precise dielectric-constant and hysteresis-loops measurements at very low heating and cooling rates ($\sim 0.5\,^{\circ}$C/h) near $T_c \approx 22.0\,^{\circ}$C in single crystals of triglycine selenate reveal previously unobserved discontinuities and a very small thermal hysteresis ($\Delta T \approx 0.05\,^{\circ}$C), indicative of a first-order transition very close to a tricritical point. The set of tricritical exponents $\beta \approx \frac{1}{4}$, $\delta \approx 5$, $\gamma \approx 1$, borne out by present data, and $\alpha \approx \frac{1}{2}$ (from Ema's specific-heat data) describe very well the observed behavior in the vicinity of the phase transition.

Triglycine selenate[1] [$(NH_2CH_2COOH)_3H_2SeO_4$], hereafter TGSe, is a well-known ferroelectric material pertaining to the triglycine sulfate (TGS) family which undergoes a typical order-disorder transition at about $T_c \approx 22\,^{\circ}$C, the space group of the lower-temperature phase being $P2_1$ and that of the higher-temperature phase $P2_1/m$. The main features of the phase transition in TGSe are like those of other members of the same ferroelectric family, and, up to the present, it has been generally considered as a second-order,[2] or continuous, phase transition. Some prominent characteristics of the TGSe transition make it worth further scrutiny. Its specific-heat peak[3,4] is about six times larger than the specific-heat peak of TGS, which may be taken as an indication that the transition is close to first order, if not first order. Also, in contrast to TGS, a moderate amount of deuteration[5] induces a clear discontinuity at the transition, accompanied by sizable thermal hysteresis. The fact that both deuteration and hydrostatic pressure are known to influence the character of the transition has led Okada and Suzuki[6] to investigate a possible tetracritical point in this crystal, which, according to them, could be attained at $p \approx 2.3$ kbar and $x = 0.38$ (deuterium concentration).

In this work we report precise dielectric-constant and hysteresis-loop measurements, performed at very low heating and cooling rates ($\sim 0.5\,^{\circ}$C/h) in the vicinity of the phase transition, from which we conclude that the phase transition of TGSe is discontinuous (first order) at ambient pressure and zero deuteration, with a small thermal hysteresis $\Delta T \approx 0.05\,^{\circ}$C. In addition, we are able to show that tricritical exponents $\beta \approx \frac{1}{4}$, $\delta \approx 5$, and $\gamma \approx 1$, obtained from our data, together with the specific-heat exponent $\alpha \approx \frac{1}{2}$, from Ema's data,[3] characterize the order-parameter behavior of the system in a certain range of temperature below T_c.

The samples were parallelepipeds with surface area (perpendicular to the b axis) ranging from 6 to 16 mm^2, and thickness (along the b axis) ranging from 2 to 6 mm, cut from a good optical quality TGSe single crystal grown from aqueous solution. Gold leaf electrodes were attached directly to the surfaces perpendicular to the ferroelectric b axis. The sample holder was well sealed within a thick-walled copper container and was immersed in a 15-l temperature-controlled oil bath regulated by a Hake model F-3, which operated in both the slow-heating and the slow-cooling modes at a rate of about 0.5 °C/h. The temperature was measured by means of a Chromel-Alumel thermocouple with a Keithley digital microvoltmeter model 196 system DMM. Capacitance (C) and loss factor (D) were measured at frequencies between 1 kHz and 1 MHz by a Hewlett-Packard precision LCR meter model HP-4284-A with very good accuracy and stability. From these data both the real and the imaginary parts of the dielectric constant could be obtained. As discussed below, the very high loss factor (of the order of unity) observable at the peak, just below the capacitance maximum, should be interpreted in terms of energy dissipation within the very low coercive-field hysteresis loops at T near and below T_c, driven by the small (~ 2 V/cm) radiofrequency signal (in fact the high-D values disappear at $T \geq T_c$), rather than in terms of intrinsic Debye relaxation behavior, which would take place only at much higher frequencies ($\sim$GHz). Hysteresis loops were observed by means of a simple Sawyer-Tower circuit with phase compensation at a frequency of 10 Hz in a Nicolet model NIC-310 digital oscilloscope with high resolution

(4000 points per loop). For reading the polarization vs field data from the loops it was important to determine precisely the true center, and this was done both by displaying the digital information on the monitor of a desktop IBM PC computer and by recording the trace of the loop with a precision Hewlett-Packard plotter. Capacitance and hysteresis-loop measurements could be taken instantaneously every second, and the resolution in temperature could be as high as 10^{-4} °C from point to point. Some of the capacitance and loss data were taken with this resolution, but no such high resolution is needed for hysteresis-loop data and, on the other hand, managing 4000 points per loop per second would become impractical. It may be noted that using relatively thick samples (~ 6 mm along the b axis) improves the reproducibility of the data.

Figure 1 shows the dielectric constant (ε) and loss factor ($D \equiv \varepsilon''/\varepsilon'$) for a relatively thick sample (4.5 mm) both heating and cooling the sample slowly at about 0.5 °C/h. It may be noticed that at temperatures above the transition the heating and cooling data points fall on top of one another. A clear discontinuity in the heating curve of $\varepsilon(T)$ at $T \approx 22.16$ °C corresponding to the peak value can be observed, accompanied by a small thermal hysteresis of about $\Delta T \approx 0.045$ °C. At $T \approx 21.16$ °C, 1 °C below the peak, another, less pronounced discontinuity shows up in the heating curve accompanied by a thermal hysteresis of about $\Delta T \approx 0.10$ °C. Discontinuities appear also in the curves of $D(T)$ at the same two temperatures, but the peak value of $D(T)$ is located at the lower one, which is displaced by about 1 °C with respect to the peak value of $\varepsilon(T)$. $D(T)$ drops discontinuously to a near-zero value just above the peak value of $\varepsilon(T)$. The peak values of D are about 0.5 and 0.7 for heating and cooling, respectively. Since these high values can be expected for normal Debye behavior[7] only near the relaxation frequency ($\omega \sim 2\pi \times 10^9$ s^{-1}), where $D_{\max} \sim \omega\tau \sim 1$, provided that $\varepsilon(\omega=0) \gg \varepsilon(\omega=\infty)$, we may conclude that they are due to energy dissipation within the low-coercive-field hysteresis loops driven by the low 1-kHz amplitude of the bridge oscillator at temperatures below and very close to the transition temperature. If this is the case, one would expect D to be proportional (for $E_c \leq E_0$, the driving field amplitude) to the area enclosed by the loops, roughly proportional to the spontaneous polarization after reaching the maximum, and near zero after the transition to the paraelectric phase is accomplished. The fact that D drops discontinuously to zero at the transition may be taken as an indication that the spontaneous polarization also drops discontinuously to zero at the transition. Subsequent measurements of spontaneous polarization vs temperature through the transition confirmed this interpretation and showed that the ratio of $D_{\max}$ at $\Delta T = 1$ °C below the transition to D just below transition is roughly the same as the ratio of $P_s^2(\Delta T = 1)$ to $P_s^2(\Delta T = 0) = (P_s^*)^2$. Measurements on good-quality single crystals of triglycine sulfate under identical conditions showed no noticeable discontinuity in a large peak with $\varepsilon_{\max} = \varepsilon(T \approx T_c) \approx 2.8 \times 10^5$.

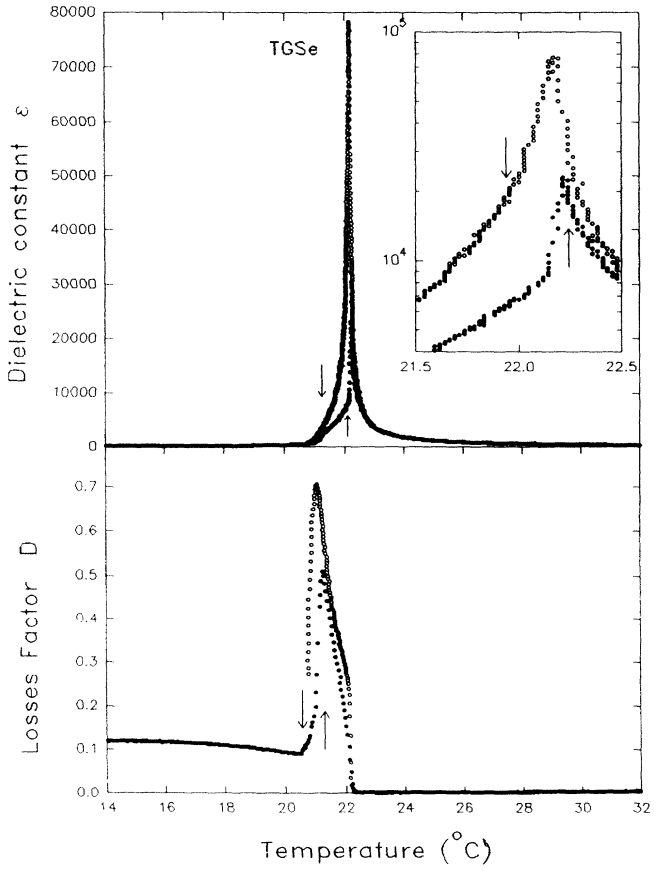

FIG. 1. Dielectric constant (ε) and dissipation factor (D) of TGSe as a function of temperature ($f = 1$ kHz) [heating (●) and cooling (○)].

Figure 2 gives the inverse of the dielectric constant $\varepsilon^{-1}(T)$, and the spontaneous polarization $P_s(T)$, measured at 10 Hz as a function of temperature in the vicinity of the transition. It can be seen that the spontaneous polarization loops suddenly to almost zero at about the same temperature as the transition discontinuity in $\varepsilon^{-1}(T)$. Furthermore, the ratio of the slopes of $\varepsilon^{-1}(T)$ vs T below and above the transition $[(1/C_-)/(1/C_+) \approx 4.5]$ is close to the value of 4 corresponding to tricritical-point behavior and considerably higher than the value of 2 pertaining to a standard critical point. The behavior of the spontaneous polarization $P_s(T)$, obtained from hysteresis loops under slow cooling, indicates a discontinuous drop at about the same temperature as the discontinuity in the dielectric constant. It may be noted that due, at least in part, to imperfect phase compensation of the hysteresis loops some amount of rounding at the transition is almost unavoidable. The estimated discontinuous jump in spontaneous polarization from these data is $P_s^* \approx 0.90$ μC/cm^2. The saturation spontaneous polarization $P_{s0} = N\mu$ for TGSe has not been measured directly, as far as we know, but a fair estimate can be obtained taking into account that $P_{s0} \approx 4.20$ μC/cm^2 for TGS,[8] and that the ratios

$$N(\text{TGSe})/N(\text{TGS}) \equiv N_{\text{Se}}/N_{\text{S}} \approx 1.56 \times 10^{22}/1.5 \times 10^{22} ,$$

and

$$\mu(\text{TGSe})/\mu(\text{TGS}) = [(N_{\text{Se}}C_{\text{S}})/(N_{\text{S}}C_{\text{Se}})]^{1/2} ,$$

where $C_{Se}=4050$ K and $C_S=3650$ K are the respective Curie constants, $C=4\pi N\mu^2/k_B$. Using these data[2] we get $P_{s0}\approx 4.50\ \mu C/cm^2$, slightly larger than the value $P_{s0}\approx 4.14\ \mu C/cm^2$ used in Ref. 4. Then we can get an estimate of the maximum thermal hysteresis ΔT_{max} to be expected in terms of $p_s^*\equiv P_s^*/P_{s0}\approx 0.20$ from[9]

$$T^*/T_c=1+\Delta T_{max}/T_c=[1-(p_s^*)^{4/5}]^{-1}=1.000\,32\ , \tag{1}$$

where $T^*=295.16$ K $=22.03$ °C is the (first-order) transition temperature and $T_c=295.06$ K $=21.93$ °C the Curie temperature. The resultant value for $\Delta T_{max}=0.10$ °C is compatible with the observed thermal hysteresis $\Delta T=0.045$ °C.

The small discontinuities for TGSe in $\varepsilon(T)$ and $P_s(T)$ at the transition and the barely observable thermal hysteresis just mentioned suggest that quasitricritical behavior may be expected just below the transition temperature in this crystal. In this case the tricritical exponents for the spontaneous polarization, the critical isotherm, the inverse dielectric constant, and the specific heat would be given by

$$p_s\propto(\Delta T)^{\beta},\ \beta=\tfrac{1}{4};\ e\propto p^{\delta},\ \delta=5\ ;$$
$$\varepsilon^{-1}\propto(\Delta T)^{\gamma},\ \gamma=1;\ \Delta C_P\propto\Delta T^{-\alpha},\ \alpha=\tfrac{1}{2}\ , \tag{2}$$

instead of by $\beta=\frac{1}{2}$, $\delta=3$, $\gamma=1$, $\alpha=0$, which are the usual critical exponents for a first-order transition. These results can easily be obtained from the equation of state relating field (e), polarization (p), and temperature (T/T_c), in dimensionless units,

$$e=(T/T_c-1)p+bp^3+cp^5\cdots\quad(T\le T_c,\ p\ll 1)\ , \tag{3}$$

for the cases $b=0$ (or $b\ll cp^2$) (tricritical-point behavior) and $b>0$ ($b\gg cp^2$) (normal critical point).

Figure 3 depicts, in log-log scales, the temperature dependence of our data of spontaneous polarization for TGSe with $T_c=21.93$ °C. The value obtained for the exponent $\beta=0.26\pm0.02$ is very close to the tricritical value $\beta=\frac{1}{4}$. In the same graph the specific-heat data for TGSe of Ema[3] are plotted directly in a log-log scale. The ferroelectric contribution to the specific heat, after subtracting the background (corresponding to nonferroelectric contributions), given in Fig. 9 of Ema's paper[3] in arbitrary units has been normalized by dividing ΔC_p by the maximum value ΔC_{pm}, corresponding presumably to $\Delta T=T^*-T=0$ °C (with T^* corresponding to Ema's T_c). The value for $\alpha=0.50\pm0.02$, obtained neglecting the first few points with $\Delta T\le 0.5$ °C is in excellent agreement also with the tricritical-point value $\alpha=\frac{1}{2}$.

Finally, Fig. 4 shows the field dependence of the polarization at a temperature $T=21.92$ °C just below $T_c<T^*=T_c+\Delta T=22.03$ °C. Again, the exponent value

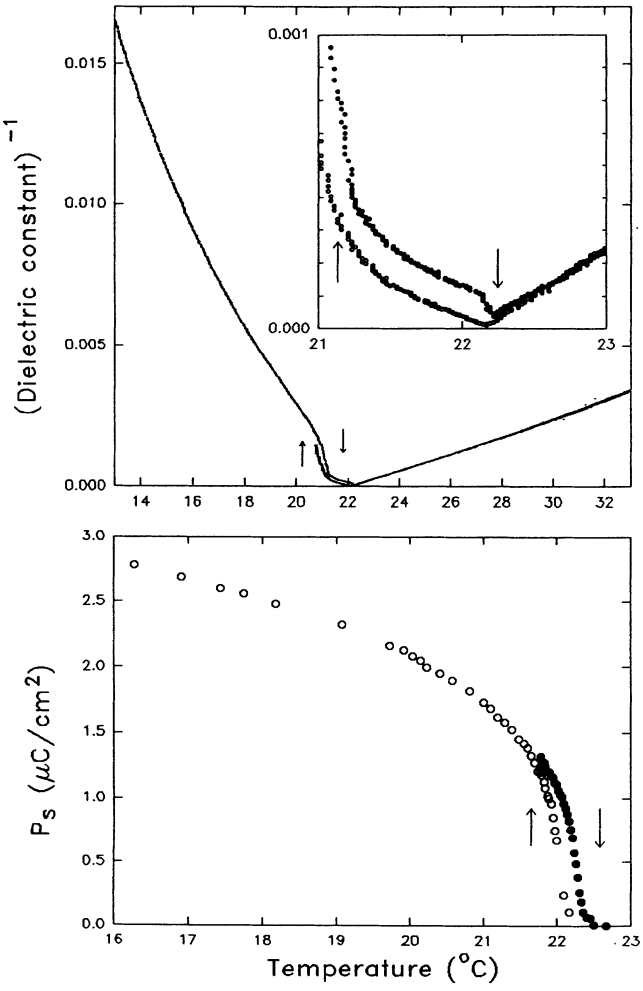

FIG. 2. Inverse dielectric constant (ε^{-1}) and spontaneous polarization(P_s) of TGSe as a function of temperature [heating (●) and cooling (○)].

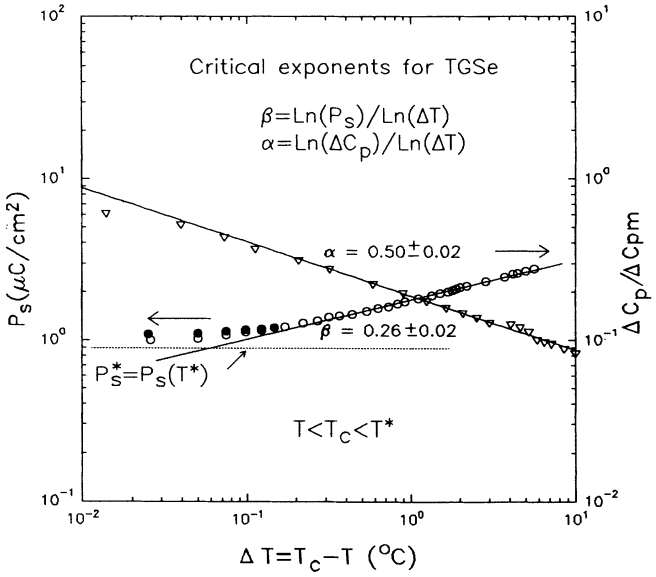

FIG. 3. Log-log plots of spontaneous polarization (this work) [heating (●) and cooling (○)] and ferroelectric specific heat [Ema's data (Ref. 3)], as a function of $\Delta T=T_c-T$ (Ema's T_c corresponds to our T^*). Numerical values for the pertinent exponents β and α are given. Spontaneous polarization data for $T>T_c$ but $T<T^*$ (corresponding to $\Delta T<0$) do not appear in this plot.

$1/\delta = 0.23 \pm 0.03$ is very close to the tricritical value $1/\delta = \frac{1}{5}$. The error quoted for $1/\delta$ corresponds to $40 < E < 150$ V/cm, since deviations towards $1/\delta = 0$ for $E \rightarrow 0$ are expected for a discontinuous transition, and also towards $1/\delta > \frac{1}{5}$ for $E \rightarrow E_{max}$ due to imperfect phase compensation of the hysteresis loop, originally compensated at $T > T_c$. $1/\delta$ has been taken, therefore, as the asymptotic value away from $E = 0$, neglecting rounding effects in the loops.

The exponent γ corresponding to $\varepsilon^{-1}(\Delta T)$ is not shown explicitly but it is clear from the asymptotic linear behavior of ε^{-1} above and below T_c that its value is very close to $\gamma = 1$, while possible logarithmic corrections very near T_c are not excluded. As should be expected the observed exponents fulfill very very well Widom's equality,

$$\beta(\delta - 1) \approx \gamma \ , \tag{4}$$

and the Griffiths equality

$$\beta(\delta + 1) \approx 2 - \alpha \ . \tag{5}$$

In summary, the results reported here clearly indicate that the ferroelectric paraelectric transition of TGSe is first order and very close to tricritical. It may be noted that the early literature on other important ferroelectric crystals, like potassium dihydrogen phosphate (KDP) and $BaTiO_3$, presented the respective transitions as second-order transitions, and only later did more precise measurements establish their first-order character. Related previous work on the TGSe phase transition[10–14] did not substantiate either the discontinuity at $T = 20.0\,^{\circ}$C or a clear quasitricritical behavior. A mean-field approach is applicable to the case of TGSe (and other uniaxial ferroelectrics) because long-range dipolar forces suppress the polarization fluctuations.

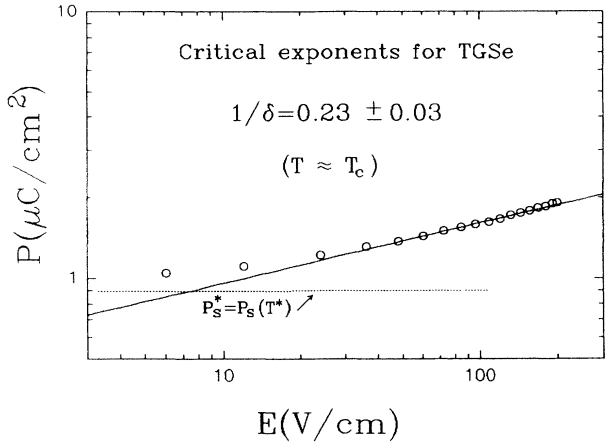

FIG. 4. Log-log plot of polarization (P) vs field (E) at $T = 21.92\,^{\circ}$C, close to the temperature corresponding to the tricritical isotherm, giving the exponent $1/\delta$.

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